PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BPCL 9860(B418)	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB 03/01419	International filing date *(day/month/year)* 01.04.2003	Priority date *(day/month/year)* 03.04.2002
International Patent Classification (IPC) or both national classification and IPC C08F10/00, C08F10/00		
Applicant BP CHEMICALS LIMITED		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
24.10.2003	29.04.2004
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Kaumann, E Telephone No. +31 70 340-3640

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB 03/01419

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-12 as originally filed

Claims, Numbers

1-8 received on 09.04.2004 with letter of 08.04.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Subject-matter

Subject-matter of the present application is a gas phase polymerization process in a fluidized bed reactor using a Ziegler-Natta catalyst, a cocatalyst and n-butyl chloride, wherein the ratio of n- butyl chloride to cocatalyst is 0,02 - 0,2., and wherein this ratio is kept constant during the polymerization.
Moreover, n-butyl chloride is added to the reactor in a molar ratio of 0,1 to 40 moles n-butyl chloride per mole transition metal catalyst compound.

The technical effect of this process is that the catalyst activity is increased and that no fouling occurs.

2. Prior art

Reference is made to the following documents:

D1: US 5,990,251 relates to a gas phase process for the polymerization of olefins using a supported Ziegler-Natta catalyst in the presence of a continuously added mono or polyhalogenated hydrocarbon (see Col. 2, lines 20 - 37 and examples). Relative amounts of halogenated hydrocarbon and cocatalyst according to the present application are disclosed in col. 3, lines 55 - 67). The use of an alkane together with the halogenated hydrocarbon is disclosed in col. 3, lines 38 - 41.
N- butyl chloride, however, is neither disclosed nor suggested. In all examples, chloroform is used.

D2: EP 0 703 246 also relates to a gas phase process for the polymerization of olefins using a supported Ziegler-Natta catalyst in the presence of a continuously added mono or polyhalogenated hydrocarbon (see claim 4, page 2, lines 46 - 54 and examples). Relative amounts of halogenated hydrocarbon and cocatalyst according to the present application are disclosed on page 3, lines 39 - 45.
The molar ratio of halogenated hydrocarbon to titanium compound is smaller that claimed in the present application (page 2, line 28 - 30).
The use of an alkane together with the halogenated hydrocarbon is disclosed on page 3, lines 32 - 33.
N- butyl chloride, however, is neither disclosed nor suggested. In all examples,

chloroform is used.

D3: EP 0 529 977 also relates to a gas phase process for the polymerization of olefins using a supported Ziegler-Natta catalyst in the presence of a mono or polyhalogenated hydrocarbon (see col. 1, lines 52 - 58, col. 4, line 55 - col. 5, line 12 and examples). Relative amounts of halogenated hydrocarbon and titanium compound according to the present application are disclosed in col. 2, lines 1 - 7).
N- butyl chloride, however, is neither disclosed nor suggested. In all examples, chloroform is used.
An organoaluminum compound may be used during the preparation of the catalyst but is not introduced into the reactor during the polymerization as cocatalysts

D4: WO 00/24789 also relates to a gas phase process for the polymerization of olefins using a supported Ziegler-Natta catalyst in the presence of a mono or polyhalogenated hydrocarbon (preferably $CHCl_3$, see page 2, lines 1 - 12 and examples).
N- butyl chloride, however, is neither disclosed nor suggested. In all examples, chloroform is used. The relative amounts of chloroform to the titanium compound are lower than 0,1, see table 1.

D5: WO 00/58374 also relates to a gas phase polymerization process in the presence of a Ziegler-Natta catalyst. The process is carried out in the presence of tetrahydrofuran and optionally of a halogenated hydrocarbon (claim 6).
N- butylchloride, however, is neither disclosed nor suggested. In all examples, chloroform is used. The relative amounts of chloroform to the titanium compound are lower than 0,1, see table 1.

3. Novelty (Article 33(2) PCT)

Regarding the distinguishing features between the subject-matter of the present application and the available prior art, outlined above, novelty can be acknowledged to present claims 1 - 8.

4. Inventive Step (Article 33(3) PCT)

D1 appears to be the closest prior art.

Distinguishing feature between D1 and the present application is, that the present application is now limited to the use of n-butyl chloride, which is neither disclosed nor suggested.
The specified and claimed molar ratio between n-butyl chloride and the transition metal catalyst compound is higher than it is the case for chloroform in the examples of D1.
Even if the claimed range for the use of chloroform in D1 overlaps with the claimed (and used) range for the use of n-butyl chloride in the present application, the comparative examples of D1 show that a higher range than used in the examples of D1 (such as claimed in the present application) is unfavourable.
Therefore, D1 leads away from the present application.

Therefore, an inventive step can be acknowledged to the present claims.

5. Article 33(4) PCT (Industrial Applicability)
Since the gas phase polymerization of olefins is an important industrial process, industrial applicability can be acknowledged to the present claims.

6. Further Remark:
The PCT application WO 02/28919 published on 11.04.2002 claims the priority date of 05.10.2000.
WO 02/28919 from the same applicant appears to disclose a similar invention.

Case 9860(2)

Claims:

1. Process for the gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst, said process comprising the addition into the reactor of an organoaluminium cocatalyst and of a monohalogenated hydrocarbon compound,

a. wherein the molar ratio of the monohalogenated hydrocarbon compound to the cocatalyst is comprised between 0.02 and 0.2, preferably between 0.02 and 0.15,

b. wherein the monohalogenated hydrocarbon compound is added to the reactor in an amount comprised between 0.1 to 40 moles of monohalogenated hydrocarbon compound per mole of transition metal of catalyst introduced into the reactor, preferably in a mole ratio comprised between 0.2 and 40, preferably 0.2 and 10, more preferably 0.25 and 5, and

c. wherein the monohalogenated hydrocarbon compound is n-butyl chloride.

2. Process according to the preceding claims wherein the Ziegler-Natta type catalyst is a silica supported Ziegler-Natta catalyst.

3. Process according to the preceding claims wherein the molar ratio of the monohalogenated hydrocarbon compound to the cocatalyst is maintained constant throughout the polymerisation.

4. Process according to any of the preceding claims wherein the sole or main olefin is either ethylene or propylene, and the optional comonomer is selected from but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene and oct-1-ene.

5. Process according to any of the preceding claims wherein the monohalogenated hydrocarbon compound is diluted in a conventional diluent like butane, pentane or hexane in an amount comprised between 0.001 and 2 mole of monohalogenated hydrocarbon compound per l of diluent.

6. Process according to any of the preceding claims wherein the monohalogenated hydrocarbon compound is not added in admixture with the catalyst.

7. Process according to any of the preceding claims wherein the catalyst is a non-prepolymerized catalyst.

8. Process according to claim 7 wherein the catalyst is a titanium magnesium silica supported catalyst which is directly introduced into the reactor.

PCT/GB03/01419
Claudine LALANNE-MAGNE et al.
Attorney Docket No. 01435.0193

ANNEXES TO THE PRELIMINARY EXAMINATION REPORT

(ARTICLE 34 AMENDMENTS)

Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

REQUEST FOR SUBSTITUTION OF REPLACEMENT SHEETS

Please substitute the attached replacement pages 1 and 2 of the claims containing the Article 34 Amendments for pages 13 and 14 of the claims in the enclosed as-filed PCT application. It is respectfully requested that the claims in the substitute pages be examined during examination of the patent application. Claims 1-8 are currently pending.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

By: _____
Ernest F. Chapman
Reg. No. 25,961

Enclosures
EFC/FPD/blc

Claims:

1. Process for the gas-phase (co-)polymerisation of olefins in a fluidised bed reactor using a Ziegler-Natta type catalyst, said process comprising the addition into the reactor of an organoaluminium cocatalyst and of a monohalogenated hydrocarbon compound, wherein the molar ratio of the monohalogenated hydrocarbon compound to the cocatalyst is comprised between 0.02 and 0.2, preferably between 0.02 and 0.15.

2. Process according to claim 1 wherein the monohalogenated compound is chosen amongst ethyl chloride, propyl chloride, butyl chloride, pentyl chloride, hexyl chloride and heptyl chloride.

3. Process according to claim 2 wherein the additive is n-butyl chloride.

4. Process according to the preceding claims wherein the Ziegler-Natta type catalyst is a silica supported Ziegler-Natta catalyst.

5. Process according to the preceding claims wherein the molar ratio of the monohalogenated hydrocarbon compound to the cocatalyst is maintained constant throughout the polymerisation.

6. Process according to any of the preceding claims wherein the sole or main olefin is either ethylene or propylene, and the optional comonomer is selected from but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene and oct-1-ene.

7. Process according to any of the preceding claims wherein the monohalogenated hydrocarbon compound is diluted in a conventional diluent like butane, pentane or hexane in an amount comprised between 0.001 and 2 mole of monohalogenated hydrocarbon compound per l of diluent.

8. Process according to any of the preceding claims wherein the monohalogenated

hydrocarbon compound is added to the reactor in an amount comprised between 0.1 to 40 moles of monohalogenated hydrocarbon compound per mole of transition metal of catalyst introduced into the reactor, preferably in a mole ratio comprised between 0.2 and 40, preferably 0.2 and 10, more preferably 0.25 and 5.

9. Process according to any of the preceding claims wherein the monohalogenated hydrocarbon compound is not added in admixture with the catalyst.